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Polymorphism and thermodynamic properties of chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex

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ABSTRACT

A new crystalline polymorph of known chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex [RuCl(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] was obtained and characterized by various analytical methods including single-crystal and powder X-ray diffraction (XRPD) and differential scanning calorimetry (DSC) in combination with thermo-gravimetric analysis (TG-DSC). The obtained crystals of new polymorph are monoclinic, space group P2$_1$/n, with a = 11.125(4), b = 19.184(6), c = 15.946(5) Å, α = 90, β = 100.174(5), γ = 90, and Z = 4. It has been found that real melting point of the complex (M.p. = 252–253 °C) can be determined only in inert atmosphere while an apparent melting is observed in the range 142–150 °C due oxygen promoted oxidative dissociation of triphenylphosphine ligand.

1. Introduction

The ruthenium complexes based on cyclopentadienyl ligand are widely used in organic chemistry and have different applications as homo- and heterogeneous catalysts and useful materials [1–3]. The chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex [RuCl(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1**) firstly prepared by Gilbert and Wilkinson [4] is one of the most investigated and useful for synthetic chemistry ruthenium compound [5–10]. However its solid state properties are an object of several contradictions [11–15]. According to the published literature data, the experimentally observed melting temperature of **1** has been found to be different. Thus, Bruce reported the melting point determined for this compound as 131–135 °C [11] that is also supported by some textbooks [16]. Meanwhile, Wilczewski claimed that the melting at this temperature is occurring only in open capillary when the complex starts melting at 135–138 °C and completely melted at 180–200 °C, while the use of a sealed capillary results in melting point 236–248 °C [14]. Unfortunately, up to present the driving forces of these incompatibilities have not been properly understood as yet. In order to clarify this long scientific discussion, we decided to synthesize and investigate the properties of this very well known organometallic specie in solid state.

In the present work we have found that complex **1** can be crystallized in different polymorphic states: previously reported polymorph **1a** [13] and synthesized by us new polymorph **1b** reported in this communication. The properties of each polymorph in solid state have been studied by single-crystal and powder X-Ray diffraction (XRPD) and differential scanning calorimetry (DSC) involving thermogravimetric and mass-spectrometry (TG/DSC/MS) analysis.

2. Results and discussion

2.1. Syntheses

The known polymorph of the ruthenium complex [RuCl(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] **1a** was obtained by previously described

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